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## **(54) CATALYST FOR REMOVAL OF CO IN HYDROGEN-CONTAINING GAS AND METHOD FOR REMOVING CO IN HYDROGEN-CONTAINING GAS WITH SAME**

**(57) Abstract:**

**PROBLEM TO BE SOLVED:** To efficiently and selectively convert and remove CO in hydrogen-contg. gas in a relatively high temp. range and to effectively reduce the concn. of CO by carrying ruthenium and an alkali metallic compd. and/or an alkaline earth metallic compd. on a fireproof inorg. oxide carrier.

**SOLUTION:** Ruthenium and an alkali metallic compd. and/or an alkaline earth metallic compd. are carried on a fireproof inorg. oxide, carrier to obtain the objective catalyst suitable for use in production of hydrogen-contg. gas for a fuel cell. At least one selected from among titania, alumina, etc. is used as the oxide carrier. At least one selected from among K, Cs, etc. is used as the alkali metal and at least one selected from among Ba, Ca, etc. is used as the alkaline earth metal. When this catalyst is used, CO in hydrogen-contg. gas can be efficiently and selectively converted and removed in a relatively high temp. range of &ge;100°C.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention makes a principal component the catalyst which carries out conversion removal of CO alternatively from hydrogen content gas, and the hydrogen which used it, and is CO and O<sub>2</sub> at least. It is related with the removal method of CO in the hydrogen content gas to contain, and is various kinds of more detailed fuel for hydrogen manufacture [, for example, methane, or more detailed natural gas (LNG). It is related with the removal method of CO which used the catalyst for removal of CO in the hydrogen content gas which can carry out conversion removal of CO alternatively from the reformed gas obtained by steam reforming of], such as hydrocarbon system fuel, such as a propane, butane or petroleum gas (LPG), naphtha, lamp oil, and gas oil, or town gas, etc., and it.

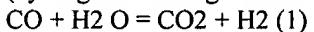
[0002]

[Description of the Prior Art] by low pollution, the power generation by the fuel cell has few energy losses, and they are advantageous also in respect of selection of an installation, extension, operability, etc. -- etc. -- since it has various advantages, attention is attracted especially in recent years Although the thing of various types is known with fuel, an electrolytic kind or electrolytic operation temperature, etc. by the fuel cell, the so-called development of the hydrogen-oxygen fuel cell (low-temperature operation type fuel cell) which uses hydrogen as a reducing agent (active material), and makes oxygen (air etc.) an oxidizer especially is progressing most, and spread will be expected increasingly from now on.

[0003] There is a thing of various types also in such a hydrogen-oxygen fuel cell according to kinds, such as an electrolytic kind and an electrode, and there are a phosphoric acid fuel cell, a KOH type fuel cell, a solid-state macromolecule type fuel cell, etc. as the typical thing. In the case of low-temperature operation type fuel cells, such as such a fuel cell, especially a solid-state macromolecule type fuel cell, platinum (platinum catalyst) is used by the electrode. However, the platinum used for the electrode has a serious trouble of a power generation performance not falling, if it is contained more than the level that has CO in fuel, since poisoning of CO is easy to be carried out, or power generation completely becoming impossible depending on concentration. Since especially activity degradation of the catalyst by this CO poisoning is as remarkable as low temperature, it becomes especially serious [ this problem ] in the case of a low-temperature operation type fuel cell.

[0004] therefore, although hydrogen pure as fuel of a fuel cell using such a platinum system electrode catalyst was desirable, from the practical point, it was cheap and excelled in keeping etc. -- it is -- it is -- various kinds of fuel [, for example, methane, already equipped fully with the public distribution system, or natural gas (LNG) It is general to use the hydrogen content gas obtained by steam reforming of fuel] for hydrogen manufacture of alcoholic system fuel, such as various kinds of hydrocarbon system fuel, such as petroleum gas (LPG), such as a propane and butane, naphtha, lamp oil, and gas oil, or a methanol, or town gas, and others etc., and the spread of the fuel cell power generation systems incorporating such a reforming facility is advanced. however -- since CO of remarkable concentration is generally contained besides hydrogen in such reformed gas -- this CO -- CO<sub>2</sub> harmless to a platinum system electrode catalyst etc. -- it converts and development of the technology of decreasing CO concentration in fuel is desired strongly It is made desirable in that case to usually reduce the concentration of CO even to the low concentration of 10 ppm or less still more preferably by 100 ppm or less preferably by 1000 ppm or less.

[0005] In order to solve the above-mentioned problem, the technology of using the water gas shift reaction (water gas shift reaction) expressed with the following formula (1) as one of the meanses which reduces the concentration of CO in fuel gas (hydrogen content gas in reformed gas) is proposed.



However, at the reaction only by this water gas shift reaction, there is a limitation in reduction of CO concentration from the restrictions on chemical equilibrium, and, generally it is difficult to make CO concentration 1% or less.

[0006] Then, as a means to reduce CO concentration to low concentration more, oxygen or oxygen content gas (air etc.) is introduced into reformed gas, and it is CO<sub>2</sub> about CO. The method of changing is proposed. However, since hydrogen is recognizing abundant existence into reformed gas in this case, if it is going to oxidize CO, hydrogen may also oxidize and CO concentration may fully be unable to decrease.

[0007] As a method for solving this problem, oxygen or oxygen content gas is introduced into reformed gas, and it is CO<sub>2</sub> about CO. It faces oxidizing and how to use the catalyst which oxidizes only CO alternatively can be considered. Although catalyst systems, such as Pt/alumina, Pt/SnO<sub>2</sub>, Pt/C, Co/TiO<sub>2</sub>, a POPUKA light, and Pd/alumina, are conventionally known

as an oxidation catalyst of CO These catalysts must also make a lot of hydrogen a sacrifice by oxidization simultaneously, in order to reduce little CO of the inside where hydrogen like reformed gas exists so much since the resistance for humidity is not enough, and a reaction temperature region is low, it is narrow and the selectivity to oxidization of CO is low to low concentration 10 ppm or less.

[0008] The manufacture method of the hydrogen content gas which does not contain CO for carrying out selection removal of CO from hydrogen enrichment CO content gas, and supplying an automotive fuel fuel cell subsystem in JP,5-201702,A is indicated. Although what supported Rh or Ru is used for alumina support as a catalyst, there is a trouble of being inapplicable only to low CO concentration.

[0009] Moreover, reducing CO concentration for the gas (CO<sub>2</sub> : they being 20 capacity % and seven to CO:10 capacity % in addition to hydrogen) reformed with the reforming vessel of a methanol to 1 capacity % using a Fe-Cr catalyst, and decreasing by the methanation using the catalyst which contains the metal further chosen from Rh, nickel, and Pd in CO as a catalyst component is indicated by JP,5-258764,A. And about CO which has not been reduced with the above-mentioned catalyst, it oxidized by plasma and has removed. Although the reformed gas which does not carry out poisoning of the platinum catalyst used as an electrode of a solid-state macromolecule type fuel cell by this method can be offered, since a plasma generator is used, there is a problem that a reactor becomes large. since [ moreover, ] reaction temperature of a methanation reaction is performed at 150-500 degrees C -- not only CO but CO<sub>2</sub> up to -- it methanates, abundant consumption of the hydrogen used as fuel is carried out, and there is also a trouble that it is unsuitable as a CO stripper from the hydrogen gas for fuel cells

[0010]

[Problem(s) to be Solved by the Invention] this invention is what was made from the above-mentioned viewpoint. CO in hydrogen content gas 100 degrees C or more preferably Conversion removal is efficiently carried out alternatively by the comparatively high temperature requirement of 100-300 degrees C. The catalyst for removal of CO in the hydrogen content gas which can fully reduce CO, and the hydrogen which used this are made into a principal component, and it is CO and O<sub>2</sub> at least. It aims at offering the removal method of CO in the hydrogen content gas to contain.

[0011] CO concentration can apply the catalyst for CO removal of this invention suitable for manufacture of the fully reduced hydrogen content gas for fuel cells.

[0012]

[Means for Solving the Problem] Wholeheartedly, as a result of research, by using for fireproof inorganic-oxide support a ruthenium and the catalyst which supported the alkali metal compound and/or the alkaline-earth-metal compound, this invention person etc. finds out that the purpose of the above-mentioned this invention can be attained effectively, and completes this invention.

[0013] That is, the summary of this invention is as follows.

(1) The catalyst for CO removal in the hydrogen content gas which comes to support a ruthenium, and an alkali metal compound and/or an alkaline-earth-metal compound to fireproof inorganic-oxide support.

(2) The catalyst for CO removal in the hydrogen content gas given [ which is a kind at least ] in (1) as which fireproof inorganic-oxide support is chosen from a titania, an alumina, a silica, and a zirconia.

(3) (1) as which alkali metal is chosen from a potassium, caesium, a rubidium, sodium, and a lithium and which is a kind at least, or the catalyst for CO removal in hydrogen content gas given in (2).

(4) (1) as which alkaline earth metal is chosen from barium, calcium, magnesium, and strontium and which is a kind at least, or the catalyst for CO removal in hydrogen content gas given in (2).

(5) Make hydrogen into a principal component and it is CO and O<sub>2</sub> at least. The removal method of CO in the hydrogen content gas characterized by using the catalyst of a publication for either of (1) - (4) as a catalyst in the method of carrying out conversion removal of CO alternatively from the hydrogen content gas to contain.

(6) Make hydrogen into a principal component and it is CO and O<sub>2</sub> at least. The removal method of CO in the hydrogen content gas given in (5) which is the mixed gas with which the hydrogen content gas to contain comes to mix oxygen content gas to the reformed gas obtained by reforming the fuel for hydrogen manufacture.

(7) The removal method of CO in the hydrogen content gas given in (6) given mixed gas is hydrogen content gas for fuel cells.

[0014]

[Embodiments of the Invention] Below, the form of operation of this invention is explained. First, the catalyst for CO removal in the hydrogen content gas of this invention is explained. Although the porosity support which consists of a thing containing these two or more sorts, such as an alumina, a silica, a silica alumina, a titania, and a zirconia, as fireproof inorganic-oxide support used for the catalyst of this invention can be mentioned, especially, a titania, an alumina, a silica, and a zirconia are desirable and especially a titania is desirable. A titania is TiO<sub>2</sub>. It says and amorphousness, a rutile type, an anatase type, etc. are used.

[0015] In order to support a ruthenium to support, for example, RuCl<sub>3</sub> and nH<sub>2</sub>O, Ru<sub>2</sub>(OH)<sub>2</sub>Cl<sub>4</sub>, 7NH<sub>3</sub> and 3H<sub>2</sub>O, and K<sub>2</sub>(RuCl<sub>5</sub>(H<sub>2</sub>O)), 2(RuCl<sub>5</sub>(H<sub>2</sub>O)) and K<sub>2</sub>(RuCl<sub>5</sub>(NO)), (NH<sub>4</sub>)<sub>2</sub>RuBr<sub>3</sub> and nH<sub>2</sub>O, Na<sub>2</sub>RuO<sub>4</sub>, and Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, OAc-nH<sub>2</sub>O, (Ru<sub>3</sub>O(OAc)<sub>6</sub>3(H<sub>2</sub>O))K<sub>4</sub> and (Ru<sub>6</sub>(CN))nH<sub>2</sub>O, K<sub>2</sub>(Ru(NO<sub>2</sub>)<sub>4</sub>(OH), (NO)), Cl<sub>3</sub> and Br (Ru<sub>6</sub>(NH<sub>3</sub>))<sub>3</sub>, (Ru<sub>6</sub>(NH<sub>3</sub>))Cl<sub>2</sub> and Br (Ru<sub>6</sub>(NH<sub>3</sub>))<sub>2</sub>, (Ru<sub>6</sub>(NH<sub>3</sub>))Cl<sub>6</sub> and H<sub>2</sub>O, and Cl (Ru<sub>5</sub>(NO)(NH<sub>3</sub>))<sub>3</sub>, (Ru<sub>3</sub>O<sub>2</sub>I<sub>4</sub>(NH<sub>3</sub>))<sub>2</sub> and RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, (Ru(OH)<sub>4</sub>(NH<sub>3</sub>))(NO<sub>3</sub>) RuCl<sub>2</sub> 4(PPh<sub>3</sub>) and -(RuClH<sub>3</sub>(PPh<sub>3</sub>))C<sub>7</sub>H<sub>8</sub>, RuH<sub>2</sub> 4(PPh<sub>3</sub>) and RuClH (CO)

(PPh<sub>3</sub>)<sub>3</sub>, RuH<sub>2</sub> 3 (PPh<sub>3</sub>) and n (RuCl<sub>2</sub>) (cod), Ru (CO)12, Ru (acac)<sub>3</sub>, n (Ru<sub>2</sub> (HCOO) (CO)), and Ru<sub>2</sub> I<sub>4</sub> 2 (p-cymene) etc. -- the catalyst manufacture liquid which is made to dissolve a ruthenium salt in water, ethanol, etc., and is obtained is used Preferably, they are RuCl<sub>3</sub> and nH<sub>2</sub>O, and Ru<sub>2</sub> at the point on handling. (OH)<sub>2</sub>Cl<sub>4</sub>, 7NH<sub>3</sub>, and 3H<sub>2</sub>O are used.

[0016] What is necessary is just to perform support to the support of a ruthenium by the usual \*\*\*\* method, the coprecipitation method, and the competitive-adsorption method using this catalyst manufacture liquid. Although what is necessary is just to select processing conditions suitably according to various methods, they should just usually contact support in catalyst manufacture liquid at room temperature -90 degree C for 1 minute to 10 hours. Although especially a limit does not have the amount of support of a ruthenium, usually, 0.05 - 10 % of the weight is desirable as a ruthenium to support, and 0.3 - 3% of the weight of the range is especially the optimal. If there are few contents of this ruthenium than a minimum, the conversion activity of CO will become inadequate, on the other hand, if it is made the rate of high support not much, the amount of the ruthenium used will become more superfluous than required, and catalyst cost will become large.

[0017] It dries, after supporting a ruthenium to support. As the dryness method, dryness with an air drying, a rotating evaporator, or a ventilation dryer is performed, for example. After dryness, usually, it is 380-500 degrees C preferably, and 350-550 degrees C is calcinated preferably for 2 to 4 hours for 2 to 6 hours. Next, an alkali metal compound and/or an alkaline-earth-metal compound are supported for the acquired ruthenium support catalyst.

[0018] In order to support an alkali metal compound, K<sub>2</sub>B<sub>10</sub>O<sub>16</sub>, KBr, KBrO<sub>3</sub>, KCN, K<sub>2</sub>CO<sub>3</sub>, KCl, KClO<sub>3</sub>, and KClO<sub>4</sub>, KF, KHCO<sub>3</sub>, KHF<sub>2</sub>, KH<sub>2</sub>PO<sub>4</sub>, and KH<sub>5</sub>2 (PO<sub>4</sub>), KHSO<sub>4</sub>, KI, KIO<sub>3</sub>, KIO<sub>4</sub>, and K<sub>4</sub>I<sub>2</sub>O<sub>9</sub>, KN<sub>3</sub>, KNO<sub>2</sub>, KNO<sub>3</sub>, KOH, KPF<sub>6</sub>, and K<sub>3</sub>PO<sub>4</sub>, KSCN, K<sub>2</sub>SO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, K salt; CsCl(s), such as K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>6</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and K(CH<sub>3</sub>COO), CsClO<sub>3</sub>, CsClO<sub>4</sub>, CsHCO<sub>3</sub>, CsI, and CsNO<sub>3</sub>, Cs salts, such as Cs<sub>2</sub>SO<sub>4</sub>, Cs(CH<sub>3</sub>COO), and Cs<sub>2</sub>CO<sub>3</sub> and CsF; Rb two B<sub>10</sub>O<sub>16</sub>, RbBr, RbBrO<sub>3</sub>, RbCl, RbClO<sub>3</sub>, PbClO<sub>4</sub>, RbI, RbNO<sub>3</sub>, Rb<sub>2</sub>SO<sub>4</sub>, Rb(CH<sub>3</sub>COO)<sub>2</sub>, and Rb<sub>2</sub>CO<sub>3</sub> etc. -- Rb salt; -- Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> -- NaB<sub>10</sub>O<sub>16</sub>, NaBr, NaBrO<sub>3</sub>, NaCN, and Na<sub>2</sub>CO<sub>3</sub>, NaCl, NaClO, NaClO<sub>3</sub>, NaClO<sub>4</sub>, NaF, NaHCO<sub>3</sub>, NaHPO<sub>3</sub>, Na<sub>2</sub>HPO<sub>3</sub>, and Na<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>3</sub>HP<sub>206</sub>, and Na two H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, NaI, NaIO<sub>3</sub>, NaIO<sub>4</sub>, NaN<sub>3</sub>, and NaN<sub>2</sub>, NaNO<sub>2</sub>, NaNO<sub>3</sub>, NaOH, Na<sub>2</sub>PO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, Na<sub>2</sub>S, NaSCN, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and Na two S<sub>2</sub>O<sub>5</sub>, Na salt; LiBO(s)2, such as Na two S<sub>2</sub>O<sub>6</sub> and Na(CH<sub>3</sub>COO) Li two B<sub>4</sub>O<sub>7</sub>, LiBr, LiBrO<sub>3</sub>, and Li<sub>2</sub>CO<sub>3</sub>, LiCl, LiClO<sub>3</sub>, LiClO<sub>4</sub>, LiHCO<sub>3</sub>, and Li<sub>2</sub>HPO<sub>3</sub>. The catalyst manufacture liquid which is made to dissolve Li salt of LiI, LiN<sub>3</sub>, LiNH<sub>4</sub>SO<sub>4</sub>, LiNO<sub>2</sub>, LiNO<sub>3</sub>, LiOH, LiSCN, Li<sub>2</sub>SO<sub>4</sub>, and Li<sub>3</sub>VO<sub>4</sub> grade in water, ethanol, etc., and is obtained is used.

[0019] In order to support an alkaline-earth-metal compound, BaBr<sub>2</sub> and Ba(BrO<sub>3</sub>)<sub>2</sub>, BaCl<sub>2</sub>, Ba(ClO<sub>2</sub>)<sub>2</sub>, and Ba(ClO<sub>3</sub>)<sub>2</sub>, Ba(ClO<sub>4</sub>)<sub>2</sub>, BaI<sub>2</sub>, Ba(N<sub>3</sub>)<sub>2</sub>, and Ba(NO<sub>2</sub>)<sub>2</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, Ba(OH)<sub>2</sub>, BaS, and BaS<sub>2</sub>O<sub>6</sub>, BaS<sub>4</sub>O<sub>6</sub> and Ba(SO<sub>3</sub>NH<sub>2</sub>)<sub>2</sub> etc. -- Ba salt; -- CaBr<sub>2</sub> -- CaI<sub>2</sub>, CaCl<sub>2</sub>, calcium(ClO<sub>3</sub>)<sub>2</sub>, and calcium(IO<sub>3</sub>)<sub>2</sub>, calcium(NO<sub>2</sub>)<sub>2</sub>, calcium(NO<sub>3</sub>)<sub>2</sub>, CaSO<sub>4</sub>, CaS<sub>2</sub>O<sub>3</sub>, and CaS<sub>2</sub>O<sub>6</sub>, calcium(SO<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>, calcium(CH<sub>3</sub>COO)<sub>2</sub>, and calcium(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> etc. -- calcium salt; -- MgBr<sub>2</sub> -- MgCO<sub>3</sub>, MgCl<sub>2</sub>, Mg(ClO<sub>3</sub>)<sub>2</sub>, and MgI<sub>2</sub>, Mg(IO<sub>3</sub>)<sub>2</sub>, Mg(NO<sub>2</sub>)<sub>2</sub>, and Mg(NO<sub>3</sub>)<sub>2</sub>, MgSO<sub>3</sub>, MgSO<sub>4</sub>, MgS<sub>2</sub>O<sub>6</sub>, and Mg(CH<sub>3</sub>COO)<sub>2</sub>, Mg(OH)<sub>2</sub> and Mg(ClO<sub>4</sub>)<sub>2</sub> etc. -- Mg salt; -- SrBr<sub>2</sub> -- SrCl<sub>2</sub>, SrI<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, SrO, SrS<sub>2</sub>O<sub>3</sub>, SrS<sub>2</sub>O<sub>6</sub>, Sr<sub>4</sub>O<sub>6</sub>, Sr(CH<sub>3</sub>COO)<sub>2</sub>, and Sr(OH) -- two etc. -- the catalyst manufacture liquid which is made to dissolve Sr salt in water, ethanol, etc., and is obtained is used

[0020] What is necessary is just to perform support to the support of a ruthenium by the usual \*\*\*\* method, the coprecipitation method, and the competitive-adsorption method using this catalyst manufacture liquid. Although what is necessary is just to select processing conditions suitably according to various methods, they should just usually contact support in catalyst manufacture liquid at room temperature -90 degree C for 1 minute to 10 hours. Although especially a limit does not have the amount of support of an alkali metal compound and an alkaline-earth-metal compound, usually, 0.01 - 10 % of the weight is desirable as a metal to support, and 0.03 - 3% of the weight of the range is especially the optimal. If there are few contents of these metals than a minimum, the conversion activity of CO will become inadequate, on the other hand, if it is made the rate of high support not much, the amount of metaled [ used ] will become more superfluous than required, and catalyst cost will become large.

[0021] It dries, after supporting the above-mentioned alkali metal compound and an alkaline-earth-metal compound. As the dryness method, dryness with an air drying, a rotating evaporator, or a ventilation dryer is performed, for example. After dryness, usually, it is 380-500 degrees C preferably, and 350-550 degrees C is calcinated preferably for 2 to 4 hours for 2 to 6 hours. In addition, as the configuration and size of the catalyst prepared by doing in this way, there is especially no limit, for example, various kinds of configurations currently generally used, such as the shape of the shape of the shape of powder, a globular shape, a grain, and a honeycomb and a foam, fibrous, blanket-like, a tabular, and a ring, and the thing of structure can use it.

[0022] After filling up a reactor with the catalyst by which manufacture was carried out [ above-mentioned ], a hydrogen reduction is performed before a reaction. Usually, under a hydrogen air current, a hydrogen reduction is 480-530 degrees C in temperature, and is performed preferably 450-550 degrees C for 1 to 2 hours for 1 to 5 hours. Hydrogen is made into a principal component at the catalyst acquired as mentioned above, and it is CO and O<sub>2</sub> at least. The gas to contain and which carries out hydrogen content is contacted, and the alternative conversion removal reaction of CO is performed. Although the removal method of CO of this invention is used suitable to remove alternatively CO in hydrogen content gas, such as reformed gas obtained by reforming the fuel for hydrogen manufacture which can be converted into the fuel gas which contains hydrogen by the reforming reaction, and is used for manufacture of the hydrogen content gas for fuel cells, it is not limited to this.

[0023] How to remove CO from reformed gas and make it into the hydrogen content gas for fuel cells hereafter, is explained.

1. Conversion removal of CO contained in the reformed gas obtained by reforming of various kinds of fuel for hydrogen manufacture in the reforming process this invention of fuel is alternatively carried out using a catalyst, and although the desired hydrogen content gas by which CO concentration was fully reduced is manufactured, the reforming process for obtaining this reformed gas can perform by arbitrary methods, such as a method enforced or proposed in the conventional fuel cell system, as shown below. Therefore, in the fuel cell system beforehand equipped with the reformer, you may prepare reformed gas, using it as it is.

[0024] As fuel used as a raw material of this reforming reaction Various kinds of kinds which can be converted into the fuel gas which makes hydrogen a principal component by the suitable reforming reaction, and contains CO, and the fuel for hydrogen manufacture of composition are usable. specifically for example Hydrocarbons, such as methane, ethane, a propane, and butane, or natural gas (LNG), Alcohols, such as hydrocarbon system fuel, such as naphtha, lamp oil, and gas oil, a methanol, ethanol, propanol, and a butanol, further various kinds of town gas, synthesis gas, coal, etc. can be used suitably. Although what fuel for hydrogen manufacture is used should just set among these in consideration of terms and conditions, such as a scale of a fuel cell system, and a supply situation of fuel, a methanol, methane or LNG, a propane or LPG, naphtha or low-grade saturation carbon, town gas, etc. are usually used suitably.

[0025] As the aforementioned reforming reaction, although a steam-reforming reaction (steam reforming) is the most common, depending on a raw material, more general reforming reactions (for example, various catalytic-reforming reactions, such as thermal-reforming reactions, such as a pyrolysis, and catalytic cracking, a water gas shift reaction, partial oxidation reforming, etc.) are also applicable suitably. You may use in that case, combining the reforming reaction of a different kind suitably. For example, may combine a steam-reforming reaction and partial oxidation to compensate a part for this endothermic, since it is generally endothermic reaction, CO which carries out a byproduction by the steam-reforming reaction etc. is made to react with H<sub>2</sub>O using a water gas shift reaction, and a steam-reforming reaction is CO<sub>2</sub> beforehand about the part. H<sub>2</sub> Various kinds of combination, such as converting, is possible.

[0026] Even if such a reforming reaction is difficult for suppressing the byproduction of CO completely and generally uses a water gas shift reaction although it selects a catalyst, a reaction condition, etc. so that the yield of hydrogen may become as large as possible, there will be a limitation in reduction of CO concentration in reformed gas. It is actually a following formula (2) or a following formula (3) because of the suppression of the yield of hydrogen, and the byproduction of CO about the steam-reforming reaction of hydrocarbons, such as methane. : CH<sub>4</sub> + 2H<sub>2</sub>O → 4H<sub>2</sub> + CO<sub>2</sub> (2)

C<sub>n</sub>H<sub>m</sub> + 2nH<sub>2</sub>O → (2 n+m/2) H<sub>2</sub>+nCO<sub>2</sub> (3)  
It is desirable to select terms and conditions so that it may come out and the reaction expressed may occur with as sufficient selectivity as possible.

[0027] Moreover, about the steam-reforming reaction of a methanol, it is the following formula (4) similarly. : CH<sub>3</sub>OH + H<sub>2</sub>O → 3H<sub>2</sub>+ CO<sub>2</sub> (4)

It is desirable to select terms and conditions so that it may come out and the reaction expressed may occur with as sufficient selectivity as possible. Furthermore, even if it carries out conversion reforming of CO using the water gas shift reaction expressed with the aforementioned (1) formula, since this water gas shift reaction is static reaction, CO of remarkable concentration remains. Therefore, it is CO<sub>2</sub> besides a lot of hydrogen in the reformed gas by such reaction. CO of an unreacted steam etc. and a some will be contained.

[0028] As a catalyst effective in the aforementioned reforming reaction, various things are known according to the kind of raw material (fuel), the kind of reaction, or the reaction condition. When some in it are illustrated concretely, as a catalyst effective in steam reforming, such as a hydrocarbon and a methanol For example, a Cu-ZnO system catalyst and Cu-Cr<sub>2</sub>O<sub>3</sub> A system catalyst, a support nickel system catalyst, A Cu-nickel-ZnO system catalyst, a Cu-nickel-MgO system catalyst, a Pd-ZnO system catalyst, etc. can be mentioned, and a support Pt system catalyst, a support nickel system catalyst, etc. can be mentioned as a catalyst effective in the catalytic-reforming reaction and partial oxidation of hydrocarbons, for example.

[0029] There is especially no limit also as a reformer, and although things of arbitrary form, such as what is regularly used by the conventional fuel cell system etc., are applicable, since many reforming reactions, such as a steam-reforming reaction and a decomposition reaction, are endothermic reaction, generally the good reactor or good reactors of heat supply nature (heat exchanger type reactor etc.) are used suitably. Although there are a polysiphonous-type reactor, a plate fin type reactor, etc. and there is heating by the catalyzed combustion which uses heating by the burner etc., the method by the heat carrier, and partial oxidation, for example etc. as a method of heat supply as such a reactor, for example, it is not limited to these.

[0030] What is necessary is just to define the reaction condition of a reforming reaction suitably, since it changes with other conditions, such as a raw material to be used, a reforming reaction, a catalyst, a kind of reactor, or a reaction method. anyway, it is desirable to select terms and conditions so that the invert ratio of a raw material (fuel) may be made large enough to 100% or about 100% desirable -- and the yield of hydrogen may become as large as possible Moreover, you may adopt the method which separates and recycles an unreacted hydrocarbon, unreacted alcohol, etc. if needed. Moreover, if needed, or it generated, it is CO<sub>2</sub> of a sheep reaction. You may remove moisture etc. suitably.

[0031] Thus, there are many hydrogen contents and the desired reformed gas with which fuel components other than hydrogen, such as a hydrocarbon and alcohol, were fully reduced is obtained. In addition, it is suitable to usually make preferably 0.10 mols or less of CO concentration in the reformed gas obtained into 0.04 mols or less to a hydrogen 1 mol, and the burden of a reaction becomes so light about inversion removal of subsequent CO such by adjusting to low concentration comparatively in CO concentration in the stage of this reforming process.

[0032] In addition, it is CO<sub>2</sub> when the catalyst of this invention is used. It is CO<sub>2</sub> although good results are shown in alternative inversion removal of CO also to the low hydrogen gas of a content. Good results are acquired also on conditions with many contents. then, this invention -- setting -- a fuel cell system -- setting -- general CO<sub>2</sub> The reformed gas 2 of concentration, i.e., CO, five to 33 capacity % -- ten to 25 capacity % and the reformed gas made still more desirable 15-20 capacity % content are used preferably

[0033] Moreover, if the catalyst of this invention is used, CO concentration can also reduce effectively CO concentration in low (below 0.6 capacity %) hydrogen gas, and can also reduce effectively CO concentration in hydrogen gas with high (0.6 to 2.0 capacity %) CO concentration.

2. Use for fireproof inorganic-oxide support as a catalyst a ruthenium and the catalyst which comes to support an alkali metal compound and/or an alkaline-earth-metal compound in the method of the alternative inversion removal process this invention of CO. It is CO<sub>2</sub> in hydrogen content gas by using this catalyst. In the temperature region containing the comparatively high temperature of 60-260 degrees C, selection inversion removal of CO can be efficiently performed also on conditions which exist more than 15% capacity. Moreover, like oxidation reaction of the hydrogen of the side reaction which occurs simultaneously, the inversion removal reaction of CO is exothermic reaction, and it is effective [ a reaction ] to collect the heat which generated heat there and to utilize within a fuel cell, when raising a generating efficiency.

[0034] When using for reformed gas the hydrogen content gas which added oxygen content gas, pure oxygen (O<sub>2</sub>), air, or oxygen-enrichment air is usually used suitably. Oxygen/CO (mole ratio) is desirable, and it is appropriate for the addition of this oxygen content gas 0.5-5, and to adjust so that it may be set to 1-4 still more preferably. If large [ if this ratio is small, the elimination factor of CO will become low, and ], the consumption of hydrogen increases too much and it is not desirable.

[0035] reaction pressure -- usually -- ordinary-pressure - 10 kg/cm<sup>2</sup> G -- desirable -- ordinary-pressure - 4 kg/cm<sup>2</sup> G -- it carries out by the pressure range of ordinary-pressure - 2 kg/cm<sup>2</sup> G preferably especially Here, since regulation of High Pressure Gas Control Law will be received and the explosion limit will spread if it becomes disadvantageous economically and 10 kg/cm<sup>2</sup> G is exceeded especially, since it is necessary to enlarge power for a pressure up that much, if reaction pressure is set up not much highly, the problem that safety falls is also produced.

[0036] Usually, preferably, it is very a latus temperature requirement, and the 60 degrees C or more of the aforementioned reactions can be performed suitably, maintaining stably the selectivity to CO shift reaction of 60-260 degrees C. Since a reaction rate becomes slow at less than 60 degrees C, this reaction temperature tends to become inadequate [ the elimination factor (invert ratio) of CO ] in the range of practical simian virus (space velocity). Since the shift reaction of CO in the process of inversion removal of this CO is exothermic reaction, the temperature of a catalyst bed rises from a reaction. If the temperature of a catalyst bed becomes high too much, the selectivity of CO inversion removal of a catalyst will usually get worse.

[0037] Moreover, it is suitable for the aforementioned reaction to select GHSV (space velocity of the volume criteria to which only the supply volume velocity in reference condition and the catalyst bed to be used of distributed gas are applied) in the range of 5000-50000hr<sup>-1</sup>, and to usually, perform it. Here, when GHSV is made small, a large-sized reactor is needed, and on the other hand, if GHSV is enlarged not much, the elimination factor of CO will fall. Preferably, it selects in the range of 6000-20000hr<sup>-1</sup>.

[0038] Although the thing of various kinds of form is applicable if there is especially no limit and the above-mentioned reaction condition can be filled as a reactor used for inversion removal of this CO, since this shift reaction is exothermic reaction, in order to make a temperature control easy, it is desirable [ a shift reaction ] to use the good reactor or good reactor of removal nature of heat of reaction. Specifically, a heat-exchanges [, such as a polysiphonous type or a plate fin type, ] type reactor is used suitably. Depending on the case, it can circulate through a cooling medium in a catalyst bed, or the method of circulating a cooling medium on the outside of a catalyst bed, and being [ a cooling medium / it ] sufficient for and making it it can be adopted.

[0039] In this way, since CO concentration is fully reduced as mentioned above, the hydrogen content gas manufactured by the method of invention can fully reduce poisoning of the platinum-electrode catalyst of a fuel cell, and degradation, and it can improve sharply the life, and a generating efficiency and a power generation performance. Moreover, it is also possible to collect the heat generated by the shift reaction of this CO. Moreover, CO concentration in the hydrogen content gas containing comparatively high-concentration CO can fully be fallen.

[0040] The hydrogen content gas obtained by this invention is various kinds of H<sub>2</sub>. Various kinds of H<sub>2</sub> of a type which can use it suitably as fuel of a burned type fuel cell, and uses platinum (platinum catalyst) for the electrode of a fuel electrode (negative electrode) at least especially It can use advantageously as supply fuel to burned type fuel cells (low-temperature operation type fuel cells including a phosphoric acid fuel cell, a KOH type fuel cell, and a solid-state macromolecule type fuel cell etc.).

[0041] In addition, between the reformer (when conversion equipment is after a reformer, it is considered that the conversion equipment is also a part of reformer) of the conventional fuel cell system, and a fuel cell By incorporating the oxygen introduction equipment and the reactor according to the method of this invention Or in what already possesses oxygen introduction equipment and shift-reaction equipment, it becomes possible also by adjusting a reaction condition as mentioned above, using the aforementioned catalyst as an inversion removal catalyst of CO to constitute the fuel cell system which was superior to before all the time.

[0042]

[Example] Next, although an example explains this invention concretely, it is not restricted to these examples at all.  
[Example 1] The ethanol solution (0.0356M) of a ruthenium trichloride (hydrate) was prepared, and 50 cc of water was added in this liquid, and it considered as \*\*\*\*\*. In this \*\*\*\*\*, as support, the titania (TiO<sub>2</sub>, the Ishihara Sangyo Kaisha, Ltd. make, CR-EL, surface-area:7m<sup>2</sup> / g) was supplied, and the catalyst was riped. The ruthenium was supported so that it might become 1% of the weight (metal conversion) to the catalyst acquired.

[0043] Dryness of a catalyst was performed using the rotating evaporator. It performed at 120 degrees C and after dryness and the muffle furnace performed baking at 500 degrees C for 4 hours for 2 hours. Next, the above-mentioned ruthenium support catalyst was supplied to 100 cc of water, and KNO<sub>3</sub> is added in it and it was made to become 0.1% of the weight with K metal to the catalyst acquired. Dryness of a catalyst was performed using the rotating evaporator. It performed at 120 degrees C and after dryness and the muffle furnace performed baking at 500 degrees C for 4 hours for 2 hours.

[0044] After fabricating the prepared catalyst with the tablet fabrication vessel, preparing the configuration to 16-32 meshes and filling up one cc reactor coil with it, it carried out reduction processing at 500 degrees C among the hydrogen air current for 1 hour. Subsequently, the mixed gas of the composition shown in Table 1 at the catalyst bed was circulated in the amount of GHSV10000hr<sup>-1</sup>, and reaction pressure set to 0.1 kg/cm<sup>2</sup> G, and performed the inversion removal reaction of CO. The reaction temperature region where reactor entrance CO concentration and the reactor outlet CO concentration in this reaction become 10 ppm or less is shown in Table 1.

[0045] In addition, identification of a product was performed using the gas chromatograph. Moreover, the fixed quantity of the oxygen in an entrance and an outlet and hydrogen is CO and CO<sub>2</sub> by TCD. The fixed quantity was methanated using the methane converter and performed using FID.

[0046] [Example 2] In the example 1, the catalyst was similarly evaluated except having replaced with the gas composition which shows gas composition of an entrance to the example 2 of Table 1. A result is shown in Table 1.

[Example 3] In the example 1, the catalyst was similarly evaluated except having replaced with the gas composition which shows gas composition of an entrance to the example 3 of Table 1. A result is shown in Table 1.

[Example 4] In the example 1, except having replaced the amount of K with to 0.05% of the weight, the catalyst was prepared similarly and the catalyst was similarly evaluated except subsequently to the example 4 of Table 1 having replaced with the gas composition which shows gas composition of an entrance. A result is shown in Table 1.

[Example 5] It sets in the example 1 and is KNO<sub>3</sub>. CsNO<sub>3</sub> Except having replaced with, the catalyst was prepared similarly and the catalyst was similarly evaluated except subsequently to the example 5 of Table 1 having replaced with the gas composition which shows gas composition of an entrance. A result is shown in Table 1.

[Example 6] It sets in the example 1 and is KNO<sub>3</sub>. Ba<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> Except having replaced with, the catalyst was prepared similarly and the catalyst was similarly evaluated except subsequently to the example 6 of Table 1 having replaced with the gas composition which shows gas composition of an entrance. A result is shown in Table 1.

[Example 7] It sets in the example 1 and is KNO<sub>3</sub>. RbNO<sub>3</sub> Except having replaced with, the catalyst was prepared similarly and the catalyst was similarly evaluated except subsequently to the example 7 of Table 1 having replaced with the gas composition which shows gas composition of an entrance. A result is shown in Table 1.

[0047] [Example 1 of reference] In the example 1, the catalyst was similarly evaluated except having replaced with the gas composition which shows gas composition of an entrance to the example 1 of reference of Table 1 about the ruthenium support catalyst which did not support K. A result is shown in Table 1.

[Example 1 of comparison] It sets in the example 1 and is KNO<sub>3</sub>. Fe<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub> Except having replaced with, the catalyst was prepared similarly and the catalyst was similarly evaluated except subsequently to the example 1 of comparison of Table 1 having replaced with the gas composition which shows gas composition of an entrance. A result is shown in Table 1.

[0048] [Example 8] In the example 1, except having replaced the titania with the alumina (aluminum 2O<sub>3</sub>, the Sumitomo Chemical Co., Ltd. make, KHD-24), the catalyst was prepared similarly and the catalyst was similarly evaluated except subsequently to the example 8 of Table 1 having replaced with the gas composition which shows gas composition of an entrance. A result is shown in Table 1.

[Example 2 of reference] In the example 8, the catalyst was similarly evaluated about the ruthenium support catalyst which did not support K. A result is shown in Table 1.

[Example 9] In the example 1, except having replaced the titania with the silica (SiO<sub>2</sub>, the product made from FUJI SILYSIACHEMICAL, CARIACT G-10), the catalyst was prepared similarly and the catalyst was similarly evaluated except subsequently to the example 9 of Table 1 having replaced with the gas composition which shows gas composition of an entrance. A result is shown in Table 1.

[Example 3 of reference] In the example 9, the catalyst was similarly evaluated about the ruthenium support catalyst which did not support K. A result is shown in Table 1.

[0049]

[Table 1]

|      | 入口ガス濃度(%) |                |                |                 | 出口CO濃度が10 ppm<br>以下の反応温度域(℃) |
|------|-----------|----------------|----------------|-----------------|------------------------------|
|      | CO        | O <sub>2</sub> | H <sub>2</sub> | CO <sub>2</sub> |                              |
| 実施例1 | 1. 0      | 2. 0           | 69. 5          | 20. 0           | 100 ~ 204                    |
| 実施例2 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | 72 ~ 212                     |
| 実施例3 | 0. 1      | 2. 0           | 87. 9          | 2. 5            | 67 ~ 227                     |
| 実施例4 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | 94 ~ 227                     |
| 実施例5 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | 60 ~ 217                     |
| 実施例6 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | 99 ~ 218                     |
| 実施例7 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | 73 ~ 204                     |
| 参考例1 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | 103 ~ 233                    |
| 比較例1 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | 179 ~ 216                    |
| 実施例8 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | 120 ~ 260                    |
| 参考例2 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | 144 ~ 196                    |
| 実施例9 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | 120 ~ 160                    |
| 参考例3 | 0. 6      | 2. 0           | 74. 9          | 15. 0           | なし                           |

[0050]

[Effect of the Invention] According to this invention, it is CO<sub>2</sub>. It is possible to carry out inversion removal of CO in hydrogen content gas with many contents alternatively efficiently over a comparatively high temperature requirement, poisoning by CO of the platinum of the hydrogen pole of a hydrogen-oxygen type fuel cell can be prevented, and the stability of an output can also be raised while making a cell age. Moreover, since the temperature region which has the alternative inversion removal ability of CO of the catalyst of this invention is comparatively high, the heat generated by the shift reaction can be collected, it can utilize within a fuel cell, and a generating efficiency can be raised.

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[Translation done.]